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PROCESS FOR THE DEPOSITION OF PALLADIUM LAYERS  
[Verfahren zur Abscheidung von Palladiumschichten]

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The invention concerns a process for the deposition of palladium layers onto metal surfaces, a bath for implementing the process as well as its use.

Base metals can be protected from aggressive gases or liquids by resistant metal layers whose type is determined essentially by the application. Thus, iron/steel is protected against rust by thin layers of copper, for example, welding rod. In the electronics industry, predominantly gold is used for the protection of surfaces to be bonded or soldered and those of contacts. Silver is not generally used for protection against corrosion because of its tendency to migrate.

Nickel layers, too, can be used as protection against corrosion, for example, of copper or copper alloys. The surfaces are first surface-activated for this purpose. The article to be coated is then dipped in an acid palladium solution, so that extremely fine palladium layers are formed, on which the deposition of the nickel starts. The palladium coating is thereby not closed and very finely distributed. The surfaces look gray. The subsequent buildup of nickel seals the surface completely. But the formed nickel layers are not oxidation resistant, cannot therefore be soldered or bonded after coating and are not suitable for use as corrosion protection in circuit board technology.

For applications where the corrosion-protective layer is also to be employed as a final layer permitting bonding or soldering, noble metals are used for the most part as an anticorrosive coating. Palladium is preferred because of its relatively low noble-metal costs. A considerable number of different baths are known /2 for the deposition of palladium layers (US patent 4,424,241; US patent 3,418,143; US patent 3,754,939; DE-OS 4,201,129; GB patent 1,164,776; DE-OS 3,000,526; US patent 4,341,846; US patent 4,255,194, DE-OS 2,841,584, EP patent application 0,423,005 A1).

Described in US patent specification 4,424,241 is a process for the chemical deposition of palladium, which works at pH below 2, methanoic acid being used among other things as a reducing agent. Amines are also listed in addition to carboxylic acids as complexing agents, but there is no indication of the type of amines to be used. From comparison tests it is evident that the palladium coatings deposited from these baths are black, adhere only inadequately to the substrate and that the baths decompose

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\*Numbers in the margin indicate pagination in the foreign text

very rapidly. It is stated that there is a danger of spontaneous salt decomposition of the bath, if the concentration of the reducing agent is set too high.

In US patent specification 3,285,754, a cementative bath is described for the deposition of palladium onto copper and copper alloys and other substrates, which contains the nitrite-palladium complexes and operates in the pH range between 2 and 5. The coatings which can be produced with the described baths are extraordinarily thin and contain pores.

According to DE-OS 4,201,129, a method is described for the manufacture of a circuit board by palladium plating without current on the copper parts of the board. The palladium baths employed are known palladium coating solutions which contain, for example, hypophosphorous acid, phosphorous acid or hydrated boron compounds, but not methanoic acid. In this case, the coating-agent solutions are enriched with the reaction products arising from oxidation of the indicated reducing agents, for example, phosphite, phosphate or borate, so that the conditions of deposition are deteriorated, /3 for example, by reduced stability in the bath against spontaneous decomposition.

The problem underlying the invention is therefore to eliminate the disadvantages of the state of the art, and to find a suitable method for the deposition of excellently adhering, gloss-retaining palladium layers, which are low in pores, on metal surfaces. Furthermore, no oxidizing compounds are to form on the palladium-covered surfaces at temperatures of up to 280 °C and standing times of a few hours, so that these surfaces can be satisfactorily soldered even after storage in air for at least from 2 to 4 weeks.

The problem is solved by patent claims 1, 8 and 13. Preferred execution variants of the invention are presented in the subclaims.

It was found that palladium layers with the described advantages can be deposited from formaldehyde-free chemical palladium bath. The coating results already with a brief coating process.

A further possibility, before palladium deposition in the formaldehyde-free chemical bath, is the activation of the metal surfaces, which can consist of copper, silver, nickel and cobalt as well as their alloys with each other and/or with phosphorus or boron, in a cementative palladium bath, to which an oxidizing agent has been added in addition to the palladium salt. Any palladium salt can be used for this bath, for example, palladium sulfate, palladium nitrate or palladium perchlorate. The palladium salt concentration amounts to approximately from 0.005 to 20 g/liter, preferably from 0.1 to 2.0 g/liter.

Usable as oxidizing agents, which can be added in a concentration of from 0.01 to 100 g/liter, preferably from 0.2 g/liter to 5.0 g/liter, are for example peroxodisulfates, perchlorates, /4 chlorates, perborates, periodates, peroxides, such as hydrogen peroxide and/or nitrates of alkali or alkaline earth metals or of ammonium.

An acid salt can be added to the cementative bath for adjustment of the same to an acid pH, for example, sodium hydrogen sulfate and/or an acid, for example, sulfuric acid or nitric acid.

Preferred applications for the chemical deposition of palladium are circuit-board technology, furthermore the manufacture of electronic components, for example, hybrid circuits, and substrates for integrated circuits, in which case the palladium layers are generally applied to those copper surfaces coated with the indicated metals, or to the copper surface itself, and the manufacture of microelectrode arrays. Moreover, such palladium coatings can also be used for protection against corrosion or solder.

When the invented process is employed in circuit-board technology, the substrate surfaces consisting of the copper are first cleaned before palladium deposition. Ordinarily used for this purpose is an etching cleaning in oxidizing, acid solutions, for example, a sulfuric acid-hydrogen peroxide solution, followed by cleaning once more in an acid solution, such as a solution of sulfuric acid. The surfaces are then activated with a solution containing palladium ions, for example, an acid-salt palladium chloride solution, and then coated with nickel in commercial chemical nickel baths. In general, nickel/phosphorus layers are deposited in this case by the use of solutions for deposition, which contain sodium hypophosphite or hypophosphorous acids as reducing agents.

However, nickel/boron layers or layers of pure nickel can also be deposited. In the place of nickel, it is also possible to deposit cobalt or its alloys with phosphorous or boron or nickel/cobalt alloys or their alloys with phosphorus or boron.

Thereafter, the surfaces can in one case be dried and then /5 submitted to pretreatment in a cementative palladium bath and then treatment with the formaldehyde-free chemical palladium bath, or treated immediately with the formaldehyde-free palladium bath without pretreatment with the cementative palladium bath. It is also possible merely to rinse the surfaces and then to coat them with palladium in the formaldehyde-free chemical palladium bath without further drying steps, with or without pretreatment using the cementative palladium bath.

Technically usable coatings, exhibiting the initially mentioned properties, with an immersion time in the formaldehyde-free

chemical bath of only 5 minutes. The thickness of the deposited layer amounts in this case to only approximately 0.2  $\mu\text{m}$ .

The bath contains essentially a palladium salt, one or more nitrogenated complexing agents and methanoic acid or methanoic acid derivatives. The pH of the solution lies above 4, preferably in the range of from 5 to 6.

Any palladium compounds can be used as palladium salts, for example, palladium chloride, palladium sulfate, palladium nitrate or palladium acetate.

Not only methanoic acid itself is suitable as a reducing agent. Its derivatives, for example, the esters of this acid, such as methanoic acid ethyl ester, the substituted and unsubstituted amides, such as formamide and N,N-dimethyl formamide, the salts of methanoic acid, for example, sodium formate, addition compounds and activated formic acids, such as orthoformic acid, can be used.

Usable cations of the methanoic acid salts (formates) include, for example, the elements of the first, second and third main groups, especially lithium, sodium, potassium, magnesium, calcium and aluminum. Also usable in addition are those formates containing ammonium or quaternary ammonium compounds.

The utilization of methanoic acid or methanoic acid derivatives as reducing agents in the process is advantageous, because these compounds, in contrast to formaldehyde, are not injurious to health and because no harmful by-products as they are oxidized during palladium deposition, but merely hydrogen and carbon dioxide arise. Carbon dioxide does not concentrate in the solution during the use of an acid formaldehyde-free chemical bath, and hydrogen escapes from the bath spontaneously. /6

Preferred for use as nitrogenated complexing agents are primary, secondary or tertiary amines or polyamines. For example, the compounds ethylenediamine, 1,3-diaminopropane, 1,2-bis(3-aminopropylamino)-ethane, 2-diethylaminoethylamine and diethylenetriamine may be used.

It is furthermore possible to use, as complexing agents, diethylenetriaminopentaacetic acid, nitroacetic acid, N-(2-hydroxyethyl)-ethylenediamine, ethylenediamino-N,N-diacetic acid, 2-dimethylamino)-ethylamine, 1,2-diaminopropylamine, 1,3-diaminopropylamine, 3-(methylamino)-propylamine, 3-(dimethylamino)-propylamine, 3-(diethylamino)-propylamine, bis(3-aminopropyl)-amine, 1,2-bis(3-aminopropyl)-alkylamine, diethylenetriamine, triethylenetetramine, tetraethylpentamine, pentaethylene hexamine and any mixtures of these nitrogenated complexing agents.

The complexing-agent content in the bath depends upon the palladium content. Typically, molar ratios of complexing agent to palladium of from 5 to 50 to 1 are used, in which case the complexing-agent content of the bath amounts to from 0.05 g/liter to 100 g/liter.

The pH of the coating solution lies above 4. At pH values below 4, the solution becomes unstable and tends to decompose automatically with the development of hydrogen. Whereas, in particular, poorly adhering and dark palladium layers are obtained on the metal surfaces when the pH drops slightly below 4, the palladium will even precipitate from the solution at pH values below approximately 2. In this case, black and inadequately adhering precipitates [7] are obtained on the substrate.

The preferred pH of the coating solution lies in the range of from 5 to 6. At pH values above 7, there is an increase in the tendency of the palladium to be deposited onto the metal surfaces cementatively, i.e. without a high gloss, and firmly adherent. Furthermore, alkaline coating solutions attack the organic resist films applied to the circuit boards, for example, solder stop masks.

In the case of baths with high deposition rates, which is achieved with a palladium concentration in excess of 2 g/liter and high bath temperature, for example, above 50 °C, or a bath loading (article surface per bath volume) above 2 dm<sup>2</sup>/liter, it is expedient to add stabilizers in a concentration of from 0.1 to 100 milligrams/liter. Such stabilizers are compounds of the elements sulfur, selenium, tellurium, copper, nickel, iron and chromium, for example, mercaptobenzothiazole, potassium selenocyanate, thiorurea and potassium ferrocyanate.

It was further possible to determine that the stability of the baths could be increased by passing inert gases, for example, air or nitrogen, through them.

With the invented process it is possible to deposit highly pure, ductile palladium coatings at a rate of up to 5 µm/hour. During palladium deposition, the layer depth increases linearly with time. It is therefore also possible to deposit thick palladium layers with the invented bath.

The deposition is carried out preferably in conventional dipping installations, in which the substrates to be treated are immersed in the bath solutions present in the containers in an essentially vertical direction. It is also conceivable, however, for the substrates to be moved through a treatment plant in a horizontal direction and thereby to come at least partly into contact /8

with the bath solutions, for example, in a metallization plant for the selective metallization of contact surfaces on circuit boards.

The following examples serve to explain the invention.

I) Formaldehyde-free chemical baths

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Example 1:

A copper plate was coated in the conventional manner with a chemical nickel/phosphorus layer and then dried. The dried plate was layered with palladium using a bath with the following composition:

Palladium acetate	0.05 moles/liter
Ethylenediamine	0.1 moles/liter
Sodium formate	0.2 moles/liter
Succinic acid	0.15 moles/liter

pH adjusted to 5.5 using methanoic acid

Temperature: 67 °C

After half an hour, the palladium coating exhibited a depth of 1.7 µm. The freedom of the coating from pores was demonstrated with the salt-spray test commonly used for determination of the corrosion resistance of coatings.

Example 2:

A copper plate was coated in the conventional manner with a galvanic layer of mat nickel and then dried. The dried plate was layered with palladium using a bath with the following composition:

Palladium sulfate	0.01 moles/liter
Ethylenediamine	0.2 moles/liter
Sodium formate	0.3 moles/liter
Succinic acid	0.2 moles/liter

pH adjusted to 5.8 using methanoic acid

Temperature: 63 °C

After an exposure time of one hour, the depth of the palladium layer was 3.8 µm. Pores could not be detected with the salt-spray test.

Example 3:

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A copper plate was coated in the conventional manner with a layer of galvanic nickel and then dried. The dried plate was coated with palladium using a bath with the following composition:

Palladium acetate	0.05 moles/liter
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1,2-Bis(3-aminopropylamino)-ethane      0.1 moles/liter  
Sodium formate      0.3 moles/liter  
Succinic acid      0.1 moles/liter  
pH adjusted to 5.9 using methanoic acid  
Temperature: 59 °C  
Obtained was a glossy layer with a depth of 1 µm; pores were no longer detectable.

Example 4:

A coppered circuit board was coated in the usual manner with a chemical nickel/boron layer and then dried. The circuit board was then coated with palladium in a bath having the following composition:

Palladium dichloride      0.5 moles/liter  
2-Diethylaminoethylamine      0.6 moles/liter  
Methanoic acid methyl ester      0.3 moles/liter  
Potassium dihydrogen phosphate      0.2 moles/liter

pH adjusted to 6.0 with methanoic acid  
Temperature: 70 °C

The deposition of palladium was interrupted after 10 minutes, the board rinsed and dried. A soldering test with this board produced an excellent result.

Example 5:

Example 1 was repeated. First of all, a chemical cobalt/phosphorus layer was deposited instead of a nickel/phosphorus layer. This was then coated with a layer of palladium.

A highly glossy, pore-free palladium coating was obtained. /11

Example 6:

A substrate prepared according to Example 1 was coated in a bath with the following composition:

Palladium chloride      0.01 moles/liter  
1,3-Diaminopropane      0.025 moles/liter  
Formamide      0.05 moles/liter  
Sodium citrate      0.1 moles/liter

pH adjusted with diluted hydrochloric acid to 7.0

Temperature: 80 °C

Likewise obtained was a highly glossy, pore-free palladium coating.

Example 7:

A substrate prepared according to Example 1 was coated in a bath have the following composition:

Palladium sulfate	0.025 moles/liter
Ammonium hydroxide	0.125 moles/liter
N,N-Dimethylformamide	0.05 moles/liter
Sodium boranate	0.15 moles/liter

pH adjustment with thinned ammoniac to 10.5

Temperature: 65 °C

The result was a highly glossy layer of palladium, which was free of pores.

Example 8:

A substrate produced according to Example 1 was coated in a bath having the following composition:

Palladium acetate	0.05 moles/liter	
Ethylenediamine	0.1 moles/liter	
Sodium formate	0.2 moles/liter	
Succinic acid	0.15 moles/liter	/12

pH adjustment to 7.0 with methanoic acid

Temperature: 50 °C

The result was a pore-free palladium coating with a high luster.

Example 9:

A substrate produced per Example 1 was coated in a bath with the following composition:

Palladium sulfate	0.01 moles/liter
Ethylenediamine	0.2 moles/liter
Sodium formate	0.3 moles/liter
Potassium hydrogen phosphate	0.2 moles/liter

pH adjusted to 7.0 using methanoic acid

Temperature: 70 °C

A palladium layer with a high gloss and no pores was obtained.

Example 10:

A substrate produced per Example 1 was coated in a bath with the following composition:

Palladium acetate	0.05 moles/liter
1,2-Bis(3-aminopropylamino)-ethane	0.1 moles/liter
Sodium formate	0.3 moles/liter
Succinic acid	0.1 moles/liter

pH adjusted to 7.0 using methanoic acid

Temperature: 90 °C

A palladium layer with a high gloss and no pores was obtained.

Example 11:

A substrate prepared per Example 1 was coated in a bath with the following composition:

Palladium sulfate	0.1 moles/liter	/13
Ethylenediamine	0.2 moles/liter	
Sodium formate	0.3 moles/liter	
Succinic acid	0.15 moles/liter	
Hydroxyethane sulfonic acid	0.0003 moles/liter	

pH adjustment to 8.5 with methanoic acid

Temperature: 75 °C

The result was a highly lustrous palladium layer, free of pores.

comparison test:

The test per Example 1 was repeated. However, the pH of palladium solution was set to 1.0.

The bath was not stable, but decomposed with the development of hydrogen and palladium precipitation. A black, mat coating precipitated onto the plate.

II) Pretreatment with acid cementative baths

Example 12:

A copper plate was cathodically electrolytically degreased, etched after being rinsed briefly (for a few seconds) in an acid peroxodisulfate solution and, after a second rinsing operation, coated with palladium in a bath. The bath had the following composition:

sodium hydrogen sulfate	30 g/liter
Sodium nitrate	3 g/liter
Palladium (as palladium sulfate)	0.2 g/liter
sulfuric acid	0.6 g/liter

Treatment conditions:

Temperature: 40 °C

Treatment time: 5 minutes

The plate was then coated in the palladium bath according to Example 1.

The copper plate was coated with a palladium layer having a white luster. The metal coating adhered very well (Tesa test). /14

The capacity to be soldered, measured with a wetting scale, was better than that of surfaces plated with gold. No decrease in the

capacity to accept solder could be detected after 14 days in storage. The porosity was very slight.

Example 13:

A copper plate, prepared as in Example 12, was treated in a solution with the following composition:

Sodium hydrogen sulfate	20.0 g/liter
Sodium peroxodisulfate	0.7 g/liter
Palladium (as sulfate)	0.2 g/liter
sulfuric acid	0.6 g/liter

Treatment conditions:

Temperature: 40 °C

Treatment time: 5 minutes

The copper plate was coated with a slightly gray, but shiny layer of palladium. The plate was then coated in the palladium bath per Example 1. Obtained was a palladium coating having no pores. The adhesion of the palladium was very good (Tesa test). The solderability was comparable to that in Example 12.

Example 14:

a copper plate, pretreated as in Example 12, was treated with palladium in a solution having a composition as follows:

Sodium hydrogen sulfate	50.0 g/liter
Potassium perchlorate	5.0 g/liter
Palladium (as sulfate)	0.2 g/liter

Treatment conditions:

Temperature: 40 °C

Treatment time: 5 minutes

After subsequent coating of the plate with palladium per Example 1, the plate was coated with a uniformly glossy palladium layer which exhibited the same good properties described in Example 12.

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Example 15:

Example 12 was repeated, but the copper plate was first coated with a copper/phosphorus layer before the treatment in the acid cementative palladium bath. The same good results were obtained.

Example 16:

Example 12 was repeated in an acid cementative palladium bath having the following composition:

Palladium nitrate	0.3 g/liter
Nitric acid, concentrated	30 g/liter

The same good results were obtained.

Example 17:

Example 12 was repeated in an acid cementative palladium bath with the following composition:

Sodium hydrogen sulfate	30 g/l
Sodium perborate	0.05 g/liter
Palladium (as palladium sulfate)	0.2 g/liter
sulfuric acid	0.6 g/liter

Obtained were the same good results.

Example 18:

Example 12 was repeated in an acid cementative palladium bath with the following composition:

Sodium hydrogen sulfate	30 g/liter
Hydrogen peroxide (30% by weight)	0.15 g/liter
Palladium (as palladium sulfate)	0.2 g/liter
sulfuric acid	0.6 g/liter

The same good results were obtained.

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Example 19:

To produce microelectrodes, polypropylene powder for chromatography (available from Polyscience, Inc., Warrington, USA) was first given a conventional pretreatment, activated, chemically coated with nickel and then coated with palladium using a formaldehyde-free chemical bath per Example 1.

The palladium-coated powder was then processed into tablets. For that purpose, the powder was put into a press. The powder was then pressed slowly and incrementally until the maximal pressure allowable for the pressing tool was reached.

The pressing tool with the pressed polypropylene powder was put into an oven preheated to 210 °C and heated for 30 minutes. To complete the microelectrode arrays, one end surface of the tablet thus obtained was polished and the other end surface provided with electrical contacts.

Example 20:

A silver plate was activated in an acid palladium bath with the following composition:

Palladium nitrate	0.3 g/liter
Nitric acid	6.0 g/liter

The plate was activated for 2 minutes and, after a rinsing operation, coated for 15 minutes in a palladium bath, per Example 2, with a layer of palladium coating having a depth of 1.2  $\mu\text{m}$ . The palladium coating was low in pores and prevented the migration of the silver.

Patent claims

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1. Process for the deposition of palladium layers on metal surfaces, from a formaldehyde-free chemical bath containing a palladium salt, one or more nitrogenated complexing agents and methanoic acid or methanoic acid derivatives a pH above 4.
2. Process according to claim 1, characterized by the fact that the pH of the formaldehyde-free, chemical bath lies in the range of from 5 to 6.
3. Process according to claim 1, characterized by the fact that a preceding activation step takes place in an acid cementative bath containing a palladium salt and an oxidizing agent or a mixture of oxidizing agents.
4. Process according to claim 3, characterized by the fact that peroxodisulfates, perchlorates, perborates, peroxides and/or nitrates are used as oxidizing agents.
5. Process according to one of the claims 3 and 4, characterized by the fact that the oxidizing agent or mixture of several oxidizing agents is used in concentrations of from 0.01 to 100 g/liter in the cementative bath.
6. Process according to one of the claims 3 through 5, characterized by the fact that palladium disulfate, palladium nitrate or palladium perchlorate is used, as a palladium salt in the cementative bath, in concentrations of from 0.005 to 20 g/liter of bath.
7. Process according to claim 1, characterized by metal surfaces consisting of copper, silver, nickel and cobalt as well as their alloys with each other and/or with phosphorus or boron.
8. Formaldehyde-free chemical bath for the deposition of palladium coatings onto metal surfaces, containing a palladium salt, one or more nitrogenated complexing agents and methanoic or methanoic acid derivatives at a pH above 4.

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9. Bath according to claim 8, characterized by salts, amides or esters of methanoic acid as methanoic acid derivatives.
10. Bath according to one of the claims 8 or 9, characterized by alkali salt formate, methanoic acid methyl ester, formamide or N,N-dimethylformamide as methanoic acid derivatives.
11. Bath according to one of the claims 8 through 10, characterized by primary, secondary or tertiary amines or polyamines as complexing agents containing nitrogen.
12. Bath according to one of the claims 8 through 11, characterized by the fact that the nitrogenated complexing agents are contained therein in concentrations of from 0.05 to 100 g/liter.
13. Utilization of the process according to one of the claims 1 through 7 for the production of circuit boards, electronic components, coatings for providing protection against corrosion, solder-stop coatings and/or microelectrode arrays.
14. Process for the deposition of palladium layers, characterized by individual or all new characteristics or combinations of the disclosed characteristics.
15. Formaldehyde-free, chemical bath for the deposition of palladium coatings, characterized by individual or all new characteristics or combinations of the disclosed characteristics.